Claims

1. A composition comprising

- a halogen containing polymer or copolymer in the form of an aqueous suspension or emulsion;
- d) a sterically hindered phenolic antioxidant with a melting point of more than 20° C containing a compound of formula (Ia) or (Ib)

OH
$$R_1$$
 R_2 R_3 R_3 R_3 R_3 R_3 R_3 R_3 R_2 R_3 R_3 R_3 R_3 R_3 R_3 R_3

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n is 2 or 3

R₁ is tert.-butyl, secondary bound C₃-C₁₈alkyl or C₅-C₆cycloalkyl;

 R'_1 is tert. butyl, primary or secondary bound C_1 - C_{18} alkyl, phenyl, C_7 - C_9 phenyl-alkyl or C_5 - C_6 cycloalkyl;

 R_3 is C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, C_5 - C_6 cycloalkyl or $-CH_2$ - CH_2 -CO-O- $(C_1$ - C_{18})alkyl; R'_2 is a divalent or trivalent bridging group;

R₄ is a group

HO

R₃

CH₂

CH₃

R₁

Or hydrogen;

R₂ is hydrogen, methyl or a group wherein

m is a number from 1 to 10; and

c) a thioether or thioether-ester with a melting point of more than 20° C of formula (IIa), (IIb) or (IIc)

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$$R_{11}$$
 (IIa), CH_3 R_{12} (IIb) or R_{11} (IIc) wherein

R₁₁ and R₁₂ are independently C₁-C₁₈alkyl

k is 2-4; and

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X is 2-methyl-1,2,3-propane-triyl- or 1,2,3,4-methane-tetryl-.

2. A composition according to claim 1 wherein the sterically hindered phenolic antioxidant containing a structural element of formula (Ia) or (Ib) is of formulae (IIIa), (IIIb) or (IIIc)

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$$R_1 \longrightarrow R_2 \pmod{R_2} \pmod{R_1 \longrightarrow R_2} \pmod{R_1 \longrightarrow R_2} \pmod{R_1 \longrightarrow R_3} \pmod{R_1 \longrightarrow R$$

n is 2 or 3

R₁ is tert.-butyl, secondary bound C₃-C₁₈alkyl or C₅-C₆cycloalkyl;

 R'_1 is tert. butyl, primary or secondary bound C_1 - C_{18} alkyl, phenyl, C_7 - C_9 phenylalkyl or C_5 - C_6 cycloalkyl;

 $\label{eq:R3} R_3 \text{ is } C_1\text{-}C_{18} \text{ alkyl, } C_1\text{-}C_{18} \text{alkoxy, } C_5\text{-}C_6 \text{cycloalkyl or a group} \\ -CH_2\text{-}CH_2\text{-}CO\text{-}O\text{-}(C_1\text{-}C_{18}) \text{alkyl;} \\ R'_2 \text{ is } C_1\text{-}C_{12} \text{alkylene, -S-, trimethylene-isocyanurate, or a group} \\ -CH_2\text{-}CH_2\text{-}CO\text{-}(OCH_2CH_2)_p\text{-}O\text{-}CO\text{-}CH_2CH_2\text{-} \text{ wherein p is a number from 1 to 3;} \\$

5 R₂ is hydrogen, methyl or a group

number from 1 to 10.

- 3. A composition according to claim 1 wherein the halogen containing polymer is PVC.
- 4. A composition according to claim 1 wherein in component c) both R₁₁ are C₁₂alkyl or C₁₈alkyl and the R₁₂ are C₁₂alkyl.
 - 5. A composition according to claim 1 wherein in component b) the sterically hindered phenolic antioxidant is
- 15 2-tert-butyl-4,6-dimethylphenol;
 - 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltetradec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltetradec-1'-yl)phenol, and mixtures thereof;
 - 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol),
- 20 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol)

or

(ethylenebis(oxyethylene)bis[3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate].

- 25 6. A composition according to claim 1 wherein in component b) the sterically hindered phenolic antioxidant is
 - 2-tert-butyl-4,6-dimethylphenol, 2,4-dimethyl-6-(1'-methyltetradec-1'-yl)phenol or a mixture thereof
 - and component c) is
- 30 di-lauryl-thio-di-propionate, di-stearyl-thio-di-propionate or a mixture thereof.

- 7. A composition according to claim 1 wherein in component b) the sterically hindered phenolic antioxidant is
- 2,4-dimethyl-6-(1'-methyltetradec-1'-yl)phenol and component c) is
- 5 di-lauryl-thio-di-propionate.
 - 8. A composition according to claim 1 wherein the sterically hindered phenolic antioxidant, component b) is present in an amount from 50 ppm to 2000 ppm based on the weight of the halogen containing monomer.

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- 9. A composition according to claim 1 wherein component c) is present in an amount from 50 ppm to 2000 ppm based on the weight of the halogen containing monomer.
- 10. A composition according to claim 1 wherein the ratio of component b) to component c) is from 1:10 to 10:1.
 - 11. A composition according to claim 1, which additionally contains a sterically hindered phenolic antioxidant different from that of component b), a phosphorous containing stabilizer, a 2-benzofuranone stabilizer, a sterically hindered amine light stabilizer or a UV-absorber.

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12. A process for the stabilization of halogen containing polymers against thermal degradation, which process comprises adding to the halogen containing polymer, which is in an aqueous suspension or emulsion during or after the polymerization process

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b) a sterically hindered phenolic antioxidant with a melting point of more than 20° C containing a compound of formula (la) or (lb)

$$R_4$$
 R_3 R_3

n is 2 or 3

R₁ is tert.-butyl, secondary bound C₃-C₁₈alkyl or C₅-C₆cycloalkyl;

R'₁ is tert. butyl, primary or secondary bound C₁-C₁₈alkyl, phenyl, C₇-C₉phenyl-alkyl or C₅-C₆cycloalkyl;

 R_3 is C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, C_5 - C_6 cycloalkyl or -CH₂-CH₂-CO-O-(C₁-C₁₈)alkyl; R'_2 is a divalent or trivalent bridging group;

5 R₄ is a group

HO
$$R_3$$
 R_3 R_4 or hydrogen;

R₂ is hydrogen, methyl or a group

number from 1 to 10; and

c) a thioether or thioether-ester with a melting point of more than 20° C of formula (IIa), (IIb) or (IIc)

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R₁₁ and R₁₂ are independently C₁-C₁₈alkyl

k is 2-4; and

X is 2-methyl-1,2,3-propane-triyl- or 1,2,3,4-methane-tetryl-.

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13. A process according to claim 12 wherein the components b) and c) are added towards the end of the polymerization reaction.

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- 14. A process according to claim 12 wherein the polymerization is a suspension polymerization and the components a) and b) are added as an emulsion to the slurry towards the end of the polymerization reaction.
- 15. Use of a sterically hindered phenolic antioxidant with a melting point of more than 20° C together with a thioether or thioether-ester with a melting point of more than 20° C according to claim 1 for the thermal stabilization of aqueous suspensions or emulsions of halogen containing polymers.